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A STUDY OF SUPERHEAT PROPERTY OF LIQUIDS

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ABSTRACT. This paper presents the results of the study of maximum attainable superheat temperature of eleven low-boiling organic liquids by the film superheating method. The experimental values have been compared with the theoretical values as obtainable from the Kinetic theory and also from the Statistical Mechanical theory. The difference between the theoretical and the experimental superheat values is seen to increase with the increasing molecular weight of the liquid. The Radiation length of the liquids under test have also been calculated at the theoretical maximum superheat temperature of the liquids.

INTRODUCTION

The study of superheat property of the liquid is important from the standpoint of nucleation theory and the bubble chamber.

Till now different workers have used different methods for investigating the maximum superheat temperature attainable in a liquid at atmospheric, subatmospheric and superatmospheric pressures. Amongst them the works of Wismer *et al* (1922), Harvey *et al* (1947), Glaser (1952), Briggs (1955) and Wakeshima and Takata (1958) are more important. The common purpose of all these methods was to reach the theoretical maximum superheat temperature.

These methods are hardly applicable to practical heat transfer systems in which a thin layer of the liquid in contact with the heater surface becomes strongly heated and the bulk of the liquid remains near the boiling temperature.

The method suggested by Sinha and Jalaluddin (1961) is however more practical in this context. The maximum superheat values obtained by this method is lower than that obtained by other methods. But in this method the liquid film remains in the superheated state for pretty long time, offering the scope for studying the liquid properties in the superheated state.

In the present work the method of Sinha and Jalaluddin (1961) has been followed.

THEORETICAL VALUES OF MAXIMUM SUPERHEAT TEMPERATURE

From equation of State (Kinetic Theory)

Temperley (1947) calculated the value of maximum superheat temperature of a liquid from the Van der Waals' equation of state. This equation is ordinarily

regarded as capable of offering qualitatively adequate account of the vapour liquid equilibrium. The superheated state of a liquid is a metastable state, and the end of this metastable state is represented on the P-V diagram by the Spinodal Lines. The equation of the Spinodal Line is

$$\left(\frac{dP}{dV}\right)_T = 0 \qquad .. \quad (1)$$

The Van der Waals' equation is

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT \qquad .. \quad (2)$$

$$\therefore \left(\frac{dP}{dV}\right)_T = P-\frac{a}{V^2}+\frac{2ab}{V^3}$$

Therefore for the Spinodal Line,

$$P-\frac{a}{V^2}+\frac{2ab}{V^3} = 0 \qquad .. \quad (3)$$

Now if the liquid is just capable of existing in the metastable state at zero pressure *i.e.* $P = 0$, equation (3) becomes

$$V = 2b \qquad .. \quad (4)$$

Substituting this value of V in equation (2), we get

$$Rt_m = \frac{a}{4b} \qquad .. \quad (5)$$

But we have

$$RT_c = \frac{8a}{27b} \qquad .. \quad (6)$$

where T_c = Critical temperature, and

a, b = Vander Waals' constants.

$$\therefore t_m = \frac{27T_c}{32} \qquad .. \quad (7)$$

By equation (7) the value of maximum superheat temperature for a liquid can be calculated from the knowledge of the critical temperature of the liquid at zero pressure. At $P = 1$ i.e., the atmospheric pressure, t_m will be slightly greater than the corresponding value at $P = 0$. So for mathematical simplicity t_m is calculated taking $P = 0$.

From rate Theory of Nucleation (Statistical Mechanical Theory)

A more appropriate value of t_m can be obtained from the Rate Theory of Nucleation in a superheated liquid. This theory is based on statistical mechanical considerations. The formulation of this theory was due to Volmer. It was improved upon by Becker and Doring where from we have got the present form.

The Volmer-Doring formula for calculating the limit of superheat theoretically is

$$J = z_1 \sqrt{\frac{6\sigma}{\pi m(3-b)}} \exp\left[-\frac{\lambda}{Kt} - \frac{16\pi\sigma^3}{3Kt(p_V - p_L)^2}\right] \quad .. \quad (8)$$

Where

J = The time rate of homogeneous nucleation.

$b = \frac{p_V - p_L}{p_V} = \frac{2\sigma}{p_V R_0}$, where R_0 = critical radius.

z_1 = Number of molecules in the superheated state.

λ = Latent heat of vaporization per mol. in ergs.

σ = Surface tension of the liquid at the operating temperature.

p_V = Saturated vapour pressure inside the bubble at the operating temperature.

p_L = Pressure on the liquid = 1 atmosphere $\approx 10^6$ dynes/cm^2

K = Boltzmann's constant.

m = Molecular mass

t = Temperature of the superheated liquid.

The limit of superheat is supposed to be the temperature at which $J = 1$. This is rather an arbitrarily selected value of the time rate of homogeneous nucleation, but this value is now well accepted.

EXPERIMENTAL SET-UP AND RESULTS

The same set-up as reported by Sinha and Jalaluddin (1961) has been used. The liquids investigated are carbon tetrachloride (*E.* Merck), chloroform (E. Merck), *n*-hexane (E. Merck), *n*-heptane (E.Merck), iso-butanol (E. Merck), methylene chloride (E. Merck), ethylene chloride (Riedel), diethylamine (E. Merck), methyl acetate (E. Merck, methyl formate (Riedel) and ethyl formate (Bush).

Table 1

Maximum superheat values t_m, experimental

	Liquid	Boiling point t_b°C	Max steady mercury temp. °C	Temp. drop across the wall of the bulb °C	Max. superheat temp. T_m°C	Degree of superheat $\Delta T = T_m - T_b$°C
1.	Carbon tetrachloride	76.7	159.9	12.8	147.1	70.4
2.	Chloroform	61.1	161.7	14.7	146.9	85.8
3.	*n*-Hexane	68.6	152.8	15.75	137.05	68.45
4.	*n*-Heptane	98.3	165.1	8.23	156.87	58.7
5.	Iso-butanol	107.8	177.1	13.1	164.0	56.2
6.	Methylene chloride	40.7	137.7	16.1	121.6	80.9
7.	Ethylene chloride	83.7	185.4	18.5	166.9	83.2
8.	Diethylamine	55.9	146.6	11.3	135.3	79.4
9.	Methyl acetate	56.9	157.1	13.7	143.4	86.5
10.	Methyl formate	31.9	168.7	18.7	150.0	118.1
11.	Ethyl formate	53.9	171.6	16.35	155.25	101.35

Table 2

Comparison of experimental values t_m with theoretical

	Liquids	Molecular weight	Theoretical values		Experimental value °C	Difference between theoretical and experimental value	
			Equation of state °C	Rate theory °C		Equation of state °C	Rate theory °C
1.	Carbon tetrachloride	154	196.0	223.0	147.1	48.9	75.9
2.	Chloroform	119.5	180.0	199.0	146.9	33.1	52.1
3.	*n*-Hexane	86	155.0	181.0	137.05	17.95	43.95
4.	*n*-Heptane	100	182.0	210.0	156.87	25.13	53.13
5.	Iso-butanol	74	181.0	207.0	164.0	17.0	43.0
6.	Methylene chloride	85	129.0	152.0	121.0	8.0	31.0
7.	Ethylene chloride	99	190.0	216.0	166.9	23.1	49.1
8.	Diethylamine	73	145.0	172.0	135.3	9.7	36.7
9.	Methyl acetate	74	154.0	179.0	143.4	10.6	35.6
10.	Methyl formate	60	138.0	164.0	150.0	−12.0	14.0
11.	Ethyl formate	74	155.0	181.0	155.25	−0.25	25.75

From figure 1 it is seen that the difference between the theoretical and the experimental values of t_m increase with the increasing molecular weight of the liquid.

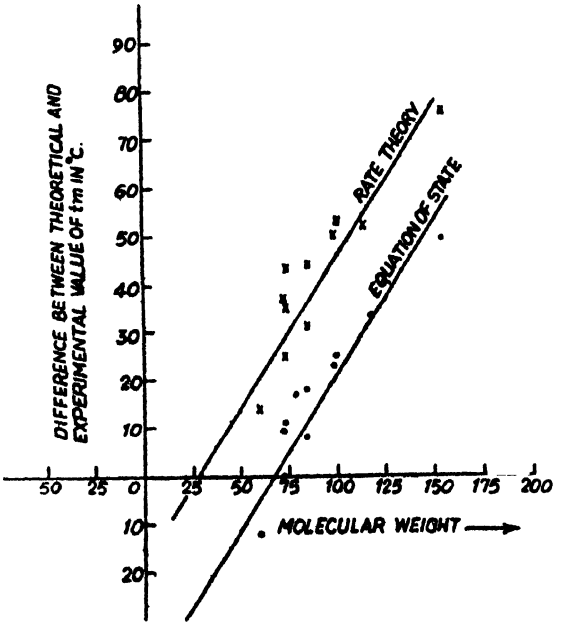

Fig. 1 Comparison of experimental and theoretical values, plotted as their differences against molecular weights.

RADIATION LENGTH

The importance of the study of superheat property of liquids has increased to a considerable amount after the development of the bubble chamber. A large number of chambers has been constructed with different liquids to study different nuclear phenomena. It is the property of a particular liquid that is most important for the study of a particular phenomenon. Raidation length is one of the most important properties of a bubble chamber liquid. It is a measure of accuracy that can be obtained in momentum determinations. On the other hand, it is also a measure of the efficiency that can be expected in pair production by gamma rays.

We shall use Bugg's (1958) modified expression for calculating radiation length (X_0). According to him,

$$\frac{1}{X_0} \quad \frac{4}{137} \cdot \frac{N}{M} \rho r_e^2 \sum_i z_i(z_i+1) \ln \frac{183}{z_i^{1/3}} \qquad .. \quad (9)$$

where N = Avogadro's number = 6.023×10^{23}

r_e = Classical radius of an electron

$$= \frac{e^2}{m_e c^2} = 2.818 \times 10^{-3} \text{ cm}$$

M = Molecular weight.

P = Density of the compound at the operating point.

Z = Atomic number.

The sum is taken over all atoms in the molecule.

Equation (9) can be further simplified, as we know that N and r_e are constants.

$$\frac{1}{X_0} = \frac{4Nr_e^2}{137} \cdot \frac{\rho}{M} \sum_i z_i(z_i+1) \ln \left(\frac{183}{z_i^{1/3}} \right)$$

$$= 1.39 \times 10^{-3} \frac{\rho}{M} \cdot \sum_i z_i(z_i+1) \ln \left(\frac{183}{z_i^{1/3}} \right) \qquad (10)$$

The value of radiation length is calculated from equation (10). Density of the liquid, ρ_t, at the operating point is calculated from the equation

$$\rho_t = [\rho_0 + 10^{-3}\alpha(t-t_0) + 10^{-6}\beta(t-t_0)^2] \qquad (11)$$

The value of ρ_0, α and β are taken from the table of critical constants.

Table 3
Radiation length

	Liquid	Formula	Theoretical max. superheat temp. t_m°C	Density at the theoretical max. superheat temp. ρ_t	Radiation length at t_m°C in cm.
1.	Carbon tetrachloride	CCl_4	223.0	1.1722	17.5
2.	Chloroform	$CHCl_3$	199.0	1.13642	18.4
3.	*n*-Hexane	C_6H_{14}	181.0	0.4880	96.5
4.	*n*-Heptane	C_7H_{16}	210.0	0.53076	89.3
5.	Iso-butanol	$(CH_3)_2CHCH_2OH$	207.0	0.6494	68.0
6.	Ethylene chloride	$ClCH_2\ CH_2Cl$	216.0	0.93198	25.4
7.	Methyl acetate	$CH_3CO_2CH_3$	179.0	0.72532	49.0
8.	Methyl formate	$HCO_2\ CH_3$	164.0	0.75129	53.0
9.	Ethyl formate	$HCO_2C_2H_5$	181.0	0.68622	60.0

The density-temperature data for methylene chloride and diethylamine was not available.

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